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CLAIMS

[Claim(s)]

[Claim 1] The high-temperature superconductivity thick-film member equipped with the interlayer of single crystal nature who was formed on the main front face of the substrate which has the main front face and consists of a single crystal or polycrystal, and said substrate and who has 0.1-micrometer or more thickness of 3 micrometers or less, and the superconduction thick film of the single crystal nature which has 0.5-micrometer or more thickness of 30 micrometers or less formed by the spreading thermal decomposition method on said interlayer.

[Claim 2] Said interlayer is a high-temperature superconductivity thick-film member according to claim 1 which has the coefficient of thermal expansion near the coefficient of thermal expansion of said superconduction thick film rather than the coefficient of thermal expansion of said substrate, and has the lattice constant near the lattice constant of said superconduction thick film rather than the lattice constant of said substrate.

[Claim 3] The high-temperature superconductivity thick-film member according to claim 1 characterized by having superconduction **** of single crystal nature further between said interlayers and said superconduction thick films.

[Claim 4] Said interlayer is a high-temperature superconductivity thick-film member according to claim 1 to 3 which has the crystal structure which inclined aslant with the include angle of 10 degrees or less to the main front face of said substrate, and is characterized by the angle of inclination of the stacking tendency within a field being 30 degrees or less.

[Claim 5] Said middle class is a high-temperature superconductivity thick-film member according to claim 1 to 4 characterized by having the monolayer or multilayer structure containing one or more sorts of oxides chosen from the group which consists of a zirconium, an ytterbium, an yttrium, and a cerium.

[Claim 6] The high-temperature superconductivity thick-film member equipped with the substrate which has the main front face and consists of a single crystal or polycrystal, superconduction **** of the single crystal nature formed on the main front face of said substrate, and the superconduction thick film of the single crystal nature which has 0.5-micrometer or more thickness of 30 micrometers or less formed by the spreading thermal decomposition method on said superconduction ****.

[Claim 7] The quality of the material of said superconduction **** and said superconduction thick film is a high-temperature superconductivity thick-film member according to claim 3 or 6 which has REBCO123 structure and is characterized by including a mutually different RE (rare earth) element as a configuration element.

[Claim 8] The high-temperature superconductivity thick-film member according to claim 7 characterized by the melting point of said superconduction **** being higher than the melting point of said superconduction thick film.

[Claim 9] The quality of the material of said substrate of a single crystal is a high-temperature superconductivity thick-film member according to claim 1 to 8 characterized by including one or more sorts chosen from the group which consists of sapphire, an ulmin acid lanthanum, magnesium oxide, and strontium titanate.

[Claim 10] The quality of the material of said substrate of polycrystal is a high-temperature superconductivity thick-film member according to claim 1 to 8 characterized by being the flexible metal which has the thickness of 200 micrometers or less, including one or more sorts chosen from the group which consists of stainless steel, Hastelloy, nickel, copper, and aluminum.

[Claim 11] It is the high-temperature superconductivity thick-film member according to claim 1 to 10 which the quality of the material of said superconduction thick film has REBCO123 structure, and is characterized by RE (rare earth) element containing a holmium.

[Claim 12] The manufacture approach of the high-temperature superconductivity thick-film member equipped with the process which forms the interlayer of single crystal nature who has 0.1-micrometer or more thickness of 3 micrometers or less on the main front face of the substrate which consists of a single crystal or polycrystal, and the process which forms the superconduction thick film of the single crystal nature which has 0.5-micrometer or more thickness of 30 micrometers or less on said interlayer using a spreading thermal decomposition method.

[Claim 13] The manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 characterized by having further the process which is after said interlayer's formation and forms superconduction **** of single crystal nature with physical vapor deposition before formation of said superconduction thick film.

[Claim 14] Said interlayer is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 or 13 characterized by being formed by physical vapor deposition.

[Claim 15] Said interlayer is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 14 characterized by being formed by the laser ablation method make the matter which irradiated laser light at the raw material and dispersed from said raw material vapor-deposit on the main front face of said substrate.

[Claim 16] Said interlayer is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 15 characterized by being formed by performing said laser ablation method after the main front face of said substrate has inclined to the field where the laser light of said raw material is irradiated.

[Claim 17] said interlayer -- a spreading thermal decomposition method -- after being formed more or being independently formed by the spreading thermal decomposition method -- the laser annealing method -- a single crystal -- the manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 or 13 characterized by being-izing and formed.

[Claim 18] Said substrate is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 which has a linear gestalt and is characterized by forming said interlayer and said superconduction thick film in order on said substrate by [of said substrate] twisting one end around the 1st roll on the other hand, and rolling round another side one end with the 2nd roll.

[Claim 19] Said substrate is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 characterized by the thing of said interlayer and said superconduction thick film for which either is formed at least while the magnitude of said substrate is two or more, and is 100cm rocked or rotating.

[Claim 20] The manufacture approach of the high-temperature superconductivity thick-film member equipped with the process which forms superconduction **** of single crystal nature with physical vapor deposition on the main front face of the substrate which consists of a single crystal or polycrystal, and the process which forms the superconduction thick film of the single crystal nature which has 0.5-micrometer or more thickness of 30 micrometers or less on said superconduction **** using a spreading thermal decomposition method.

[Claim 21] Said substrate is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 20 which has a linear gestalt and is characterized by forming said superconduction **** and said superconduction thick film in order on said substrate by [of said substrate] twisting one end around the 1st roll on the other hand, and rolling round another side one end with the 2nd roll.

[Claim 22] Said substrate is the manufacture approach of the high-temperature superconductivity thick-

film member according to claim 20 or 21 characterized by the thing of said superconduction **** and said superconduction thick film for which either is formed at least while the magnitude of said substrate is two or more, and is 100cm rocked or rotating.

[Claim 23] Said process which forms said superconduction thick film of a single crystal using a spreading thermal decomposition method is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 or 20 characterized by making it single-crystal-ize by the laser annealing method after forming a superconduction thick film with said spreading thermal decomposition method.

[Claim 24] The source of annealing in said laser annealing method is the manufacture approach of the high-temperature superconductivity thick-film member according to claim 23 characterized by being the YAG laser which has the excimer laser, or 0.5-micrometer or more wavelength of 2 micrometers or less which has 0.1-micrometer or more wavelength of 0.5 micrometers or less.

[Claim 25] The manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 or 20 characterized by performing four processings, a temporary-quenching join, this conclusion, postannealing, and oxygen annealing, to said superconduction thick film at least.

[Claim 26] The manufacture approach of the high-temperature superconductivity thick-film member according to claim 12 or 20 characterized by the raw material in said spreading thermal decomposition method containing an organic metal raw material.

[Claim 27] The manufacture approach of a high-temperature superconductivity thick-film member according to claim 12 or 20 that said superconduction thick film is formed in both sides of said substrate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] It has the superconduction property which was more excellent in the detail about a high-temperature superconductivity thick-film member and its manufacture approach, and a presentation and the organization of this invention are uniform, and it bears the big critical current which deserves practical use, and relates to the high-temperature superconductivity thick-film member suitable for especially a power application in which a long picture or a large area is possible, and its manufacture approach.

[0002]

[Description of the Prior Art] Utilization development is progressing by application of a physical-vapor-deposition technique which cultivated the high-temperature superconductivity thin film by the conventional semiconductor industry, such as the sputtering method, heat vapor codeposition, electron beam vacuum deposition, and laser vacuum deposition. In the high-temperature superconductivity thin film which has Y(yttrium) 123 system structure or RE(rare earth) 123 system structure where especially critical temperature amounts to 90K, the critical current property exceeding the critical temperature exceeding liquid nitrogen temperature (77K) or 105 A/cm² (under 77K and a self-field) is checked, and the property which exceeds completely Bi (bismuth) system silver covering high-temperature superconductivity wire rod with which utilization progressed is checked on lab level.

[0003] After development of prototypes, such as a prototype which aimed at utilization of the microwave filter used for the communication link base station of a mobile, and magnetocardiograph using a SQUID (Super conducting Quantum Interference Device) phenomenon, the element development which aimed at the high-speed computer using the Josephson effect are progressing quickly using such a high-temperature superconductivity thin film and dependability is checked the engine performance and over a long period of time compared with the conventional usual state electrical conduction device in a cost side, it is expected that commercial production progresses.

[0004] On the other hand, development of the prototype is promoted also for the so-called power applicable fields, such as a current limiter, in the cable or the magnet using the "electric resistance =0" phenomenon of superconduction. The compact and large capacity cable which can be laid to the tunnel of the existing small diameter (150-200mmphi extent) can be built without a diameter newly producing the tunnel of meter class to underground in the center of Tokyo, if the underground cable using a high-temperature superconductivity wire rod is realizable. The power of 3 times or more over the past can be transmitted, and since the ground work expense which big cities, such as Tokyo, take huge cost becomes unnecessary and a cost merit arises, development is wholeheartedly furthered by this.

[0005] Moreover, Y system and RE system thin film wire rod are very excellent in the magnetic field property of 77K compared with Bi system silver covered-wire material. For this reason, if long picture-ization of a wire rod progresses and the engine performance predetermined at proper cost can be attained, Y system and RE system thin film wire rod will become leading as a wire rod MRI (Magnetic Resonance Imaging) to which application-ization is progressing, for example with the metal system

superconduction wire rod, and for the superconduction magnets for silicon single crystal pull-up furnaces. Moreover, examination of SN rearrangement mold current limiter using a thin film is also made, and it is also examined by Bi system silver covered-wire material from which a matrix serves as stabilization material whether an unrealizable compact and highly efficient current limiter can be realized in Y system and RE system thin film.

[0006]

[Problem(s) to be Solved by the Invention] It has the description that physical vapor deposition has few presentation gaps of the high-temperature superconductivity film which formed membranes from the raw material target, and its membrane formation rate is comparatively quick also in vapor growth. For this reason, a spatter and laser vacuum deposition are applied to the purpose of the principle verification of a thin film which has the outstanding property. However, present laser and a present sputtering system have the trouble that power is small, when performing mass production of a thin film superconduction wire rod or a large area thin film.

[0007] Although it could produce commercially in electronics application of SQUID, a computer, etc. when the film which has high performance was producible to homogeneity, even if little, there was a problem fundamental for utilization that the manufacture cost in physical-vapor-deposition equipment was high.

[0008] On the other hand, in the power applicable field, although the process which can produce a thin film by low cost in large quantities especially was required, physical vapor deposition was restricted to the technique for the experiment of principle verification by the low-power output of vacuum evaporatio~~n~~ equipment power. Even if the source of laser and the source of a spatter which have high power required for the physical vapor deposition of a high-temperature superconductivity thin film continue this cause for the future, it is because the prospect of a high increase in power is limited.

[0009] this time -- as for example, the source of laser -- an output -- at most -- only the industrial laser which is about 200W can be produced commercially. For this reason, it is theoretically difficult to manufacture the thick superconduction film 5 micrometers or more at the membrane formation rate of 10 or more m/H, for example on a tape substrate with a width of face of 10mm.

[0010] As the technique of the ability to manufacture Y system superconduction thin film in large quantities, there is a spreading thermal decomposition method currently indicated by JP,4-76324,B, JP,4-76323,B, etc. Although this technique has the advantage from which the thick film to a wire rod and single crystal substrate top is obtained comparatively easily using equipment simpler than physical vapor deposition, it has the radical fault that critical current density is low, by the superconduction film produced by this technique.

[0011] For example, although J_c of 105 - 106 A/cm² (77K, 0T) extent was obtained on the single crystal, since a membranous crack, a presentation gap, etc. arose by the large area film, the formation of the large area film was difficult. Generating of a crack originates in the differential thermal expansion of a substrate and a superconduction thick film, or the mismatch of a crystal, and is produced. Moreover, the presentation gap originates in generating of the hole produced in case the unnecessary matter evaporates in the process made to single-crystal-ize by that epitaxial growth arises from on a substrate imperfectly, or heat treatment etc.

[0012] Furthermore, on the polycrystal metal substrate, the superconduction film did not carry out orientation but remained at J_c of 104 A/cm² (77K, 0T) class. It is because the superconduction thick film which grew from the polycrystal substrate does not carry out orientation of the low cause of J_c in the one direction in a field. These results, the technique of Y system superconduction thin film which is compatible in a high property, and a thick film and mass-production nature did not exist, but it was thought that application of Y thin film was difficult for power application of a superconduction cable, a current limiter, etc.

[0013] So, the purpose of this invention is offering the high-temperature superconductivity thick-film member which makes possible the long thick-film wire rod which has the conventionally difficult high superconduction property, and a large area thick film, and its manufacture approach.

[0014]

[Means for Solving the Problem] The high-temperature superconductivity thick-film member according to the aspect of affairs of 1 of this invention is equipped with the substrate, the interlayer of single crystal nature, and the superconduction thick film of single crystal nature. A substrate has the main front face and consists of a single crystal or polycrystal. An interlayer is formed on the main front face of a substrate, and has 0.1-micrometer or more thickness of 3 micrometers or less. A superconduction thick film is formed by the spreading thermal decomposition method on an interlayer, and has 0.5-micrometer or more thickness of 30 micrometers or less.

[0015] According to the high-temperature superconductivity thick-film member according to the aspect of affairs of 1 of this invention, this interlayer's coefficient of thermal expansion can be made into the thing near [substrate] a superconduction thick film by having prepared the interlayer. By this, the differential thermal expansion of a substrate and a superconduction thick film can be eased, it becomes possible to prevent a membranous crack, and large area membrane formation becomes easy.

[0016] Moreover, an interlayer's lattice constant can be made into the thing near [substrate] a superconduction thick film, and, thereby, the grid distortion by the mismatch of the crystal of a substrate and a superconduction thick film can be eased. Also by this, a membranous crack can be prevented and large area membrane formation becomes easy.

[0017] Moreover, since an interlayer can be formed with physical vapor deposition etc., an interlayer's crystal stacking tendency can be made good. For this reason, even if it forms a superconduction thick film with a spreading thermal decomposition method, the crystal stacking tendency of a superconduction thick film can be made good, and big critical current density can be obtained.

[0018] Therefore, the long thick-film wire rod and large area thick film which have the conventionally difficult high superconduction property become possible.

[0019] In addition, an interlayer's thickness was set to 0.1 micrometers or more 3.0 micrometers or less because a crystal stacking tendency would fall in less than 0.1 micrometers, if the good film of a stacking tendency was not able to be obtained but it exceeded 3.0 micrometers. Moreover, it is because a crystal stacking tendency will fall if having set thickness of a superconduction thick film to 0.5 micrometers or more 30 micrometers or less can form thickness 0.5 micrometers or more easily if a spreading thermal decomposition method is used, and it exceeds 30 micrometers.

[0020] When forming a superconduction thin film, a crystallographic axis has the property "a set and a cone are a pile to a set in ab shaft orientation within a field in the direction of a c-axis." For this reason, in this application, the crystal of "single crystal nature" means the crystal "to which ab shaft within a field was also equal to with the c-axis, namely, the direction of all crystallographics axis was equal."

[0021] In top Norikazu's aspect of affairs, preferably, the interlayer has the coefficient of thermal expansion near the coefficient of thermal expansion of a superconduction thick film rather than the coefficient of thermal expansion of a substrate, and has the lattice constant near the lattice constant of a superconduction thick film rather than the lattice constant of a substrate.

[0022] Thereby, the long thick-film wire rod and large area thick film which have the conventionally difficult high superconduction property become possible like the above.

[0023] In top Norikazu's aspect of affairs, it has superconduction **** of single crystal nature further between the interlayer and the superconduction thick film preferably.

[0024] In order that this superconduction **** may achieve the function of the nucleation at the time of growing epitaxially, the epitaxial growth of a superconduction thick film of it becomes possible on an interlayer.

[0025] In top Norikazu's aspect of affairs, the middle class has preferably the monolayer or multilayer structure containing one or more sorts of oxides chosen from the group which consists of a zirconium, an ytterbium, an yttrium, and a cerium.

[0026] Thus, an interlayer's quality of the material can be chosen suitably. In top Norikazu's aspect of affairs, preferably, an interlayer has the crystal structure which inclined aslant with the include angle of 10 degrees or less to the main front face of a substrate, and the stacking tendency within a field is 30 degrees or less of angles of inclination.

[0027] Thereby, it can consider as a good crystal stacking tendency. The high-temperature

superconductivity thick-film member according to other aspects of affairs of this invention is equipped with a substrate, superconduction **** of single crystal nature, and the superconduction thick film of single crystal nature. A substrate has the main front face and consists of a single crystal or polycrystal. Superconduction **** is formed on the main front face of a substrate. A superconduction thick film is formed by the spreading thermal decomposition method on superconduction ****, and has 0.5-micrometer or more thickness of 30 micrometers or less.

[0028] Although the complicated heat treatment approach is required of a spreading thermal decomposition method, while the thick-film formation with few presentation gaps than the case where there is no superconduction **** by giving this superconduction **** becomes easy according to the high-temperature superconductivity thick-film member according to other aspects of affairs of this invention, low temperature-ization of a crystallization process also becomes possible. Furthermore, single-crystal-izing of the superconduction thick film by complicated heat treatment and possibility of becoming unnecessary were found out. Since a presentation gap of a superconduction thick film can be prevented by this even if there is no interlayer, large area membrane formation is attained.

[0029] Therefore, the long thick-film wire rod and large area thick film which have the conventionally difficult high superconduction property become possible.

[0030] In the aspect of affairs besides the above, preferably, the quality of the material of superconduction **** and a superconduction thick film has REBCO123 structure, and contains a mutually different RE element as a configuration element.

[0031] Thereby, by changing a presentation and configuration rare earth elements of the superconduction of superconduction **** and a superconduction thick film, if the melting point of superconduction **** is made high, also in heat treatment at the time of single-crystal-izing a superconduction thick film, seed crystal will serve as an origin of a nucleation, without producing crystal decomposition, and single crystal-ization of a superconduction thick film will become easy.

[0032] In addition, "REBCO123 structure" in this application specification means that it is $0.7 \leq x \leq 1.3$, $1.7 \leq y \leq 2.3$, and $2.7 \leq z \leq 3.3$ in $\text{RExBa}_y\text{Cu}_z\text{O}_{7-d}$.

[0033] In an aspect of affairs besides the above, the melting point of superconduction **** is higher than the melting point of a superconduction thick film preferably.

[0034] Thereby, also in heat treatment at the time of single-crystal-izing a superconduction thick film, seed crystal serves as an origin of a nucleation, without producing crystal decomposition, and it becomes easy to single-crystal-ize [of a superconduction thick film] it.

[0035] In top Norikazu and other aspects of affairs, the quality of the material of the substrate of a single crystal contains preferably one or more sorts chosen from the group which consists of sapphire, an ulmin acid lanthanum, magnesium oxide, and strontium titanate.

[0036] Thus, it is possible to choose the quality of the material of a substrate suitably. In top Norikazu and other aspects of affairs, the quality of the material of the substrate of polycrystal is a flexible metal which has the thickness of 200 micrometers or less, including one or more sorts chosen from the group which consists of stainless steel, Hastelloy, nickel, copper, and aluminum preferably.

[0037] Thus, the quality of the material of the substrate of polycrystal can be chosen suitably. In top Norikazu and other aspects of affairs, preferably, a superconduction thick film has REBCO123 structure, and RE element contains a holmium.

[0038] The manufacture approach of a high-temperature superconductivity thick-film member of following the aspect of affairs of 1 of this invention is equipped with the following processes.

[0039] On the main front face of the substrate which consists of a single crystal or polycrystal first, the interlayer of single crystal nature who has 0.1-micrometer or more thickness of 3 micrometers or less is formed. And on an interlayer, the superconduction thick film of the single crystal nature which has 0.5-micrometer or more thickness of 30 micrometers or less is formed using a spreading thermal decomposition method.

[0040] According to the manufacture approach of a high-temperature superconductivity thick-film member of following the aspect of affairs of 1 of this invention, this interlayer's coefficient of thermal expansion can be made into the thing near [substrate] a superconduction thick film by having prepared

the interlayer. By this, the differential thermal expansion of a substrate and a superconduction thick film can be eased, it becomes possible to prevent a membranous crack, and large area membrane formation becomes easy.

[0041] Moreover, an interlayer's lattice constant can be made into the thing near [substrate] a superconduction thick film, and, thereby, the grid distortion by the mismatch of the crystal of a substrate and a superconduction thick film can be eased. Therefore, a membranous crack can be prevented also from this point and large area membrane formation becomes easy.

[0042] Moreover, since an interlayer can be formed with physical vapor deposition etc., an interlayer's crystal stacking tendency can be made good. For this reason, even if it forms a superconduction thick film with a spreading thermal decomposition method, the crystal stacking tendency of a superconduction thick film can be made good, and big critical current density can be obtained.

[0043] Therefore, manufacture of the long thick-film wire rod which has the conventionally difficult high superconduction property, or a large area thick film is attained.

[0044] In top Norikazu's aspect of affairs, preferably, it is after an interlayer's formation and superconduction **** of single crystal nature is formed by physical vapor deposition before formation of a superconduction thick film.

[0045] In order that this superconduction **** may achieve the function of the nucleation at the time of growing epitaxially, the epitaxial growth of a superconduction thick film of it becomes possible on an interlayer.

[0046] In top Norikazu's aspect of affairs, an interlayer is preferably formed by physical vapor deposition. An interlayer's crystal stacking tendency can be made good, by this, even if it forms a superconduction thick film with a spreading thermal decomposition method, the crystal stacking tendency of a superconduction thick film can be made good, and big critical current density can be obtained.

[0047] In top Norikazu's aspect of affairs, an interlayer is preferably formed by the laser ablation method make the matter which irradiated laser light at the raw material and dispersed from the raw material vapor-deposit on the main front face of a substrate.

[0048] Thereby, the interlayer who did self-orientation can be obtained. In top Norikazu's aspect of affairs, an interlayer is preferably formed by performing the laser ablation method, after the main front face of a substrate has inclined to the field where the laser light of a raw material is irradiated.

[0049] Thus, adoption of the substrate inclination forming-membranes method (ISD:Inclined Substrate Deposition) enables formation of the single crystal nature interlayer for enabling formation of a superconduction thick film on various substrates which have random crystal orientation. In this case, an interlayer achieves two new functions of prevention of the element diffusion from a substrate, and the formation of crystal orientation of a superconduction thick film in addition to crystal-lattice strain relaxation.

[0050] In top Norikazu's aspect of affairs, an interlayer is preferably formed of a spreading thermal decomposition method independent, or after being formed by the spreading thermal decomposition method, by the laser annealing method, it crystallizes single and is formed.

[0051] By this technique, an interlayer can be single-crystal-ized and a crystal stacking tendency can be made good.

[0052] In top Norikazu's aspect of affairs, preferably, a substrate has a linear gestalt, on the other hand, one end is twisted around the 1st roll, and an interlayer and a superconduction thick film are formed in order on a substrate by [of a substrate] rolling round another side one end with the 2nd roll.

[0053] This becomes possible to form each film in the longitudinal direction of a linear substrate in order. Either is formed even if there are few interlayers and superconduction thick films the magnitude of a substrate being two or more [100cm], and rocking or rotating a substrate preferably in top Norikazu's aspect of affairs.

[0054] This becomes possible to form each film also to a large area substrate called two or more [100cm].

[0055] The manufacture approach of a high-temperature superconductivity thick-film member of

following other aspects of affairs of this invention is equipped with the following processes.

[0056] On the main front face of the substrate which consists of a single crystal or polycrystal first, superconduction **** of single crystal nature is formed by physical vapor deposition. And on superconduction ****, the superconduction thick film of the single crystal nature which has 0.5-micrometer or more thickness of 30 micrometers or less is formed using a spreading thermal decomposition method.

[0057] Although the complicated heat treatment approach is required of a spreading thermal decomposition method, while formation of a superconduction thick film with few presentation gaps than the case where there is no superconduction **** by giving this superconduction **** becomes easy, low temperature-ization of a crystallization process also becomes possible. Furthermore, single-crystal-izing of the superconduction thick film by complicated heat treatment and possibility of becoming unnecessary were found out. Since a presentation gap of a superconduction thick film can be prevented by this even if there is no interlayer, large area membrane formation is attained.

[0058] Therefore, it becomes possible to manufacture the long thick-film wire rod which has the conventionally difficult high superconduction property, and a large area thick film.

[0059] In an aspect of affairs besides the above, preferably, a substrate has a linear gestalt, on the other hand, one end is twisted around the 1st roll, and superconduction **** and a superconduction thick film are formed in order on a substrate by [of a substrate] rolling round another side one end with the 2nd roll.

[0060] This becomes possible to form each film in the longitudinal direction of a linear substrate in order. Either is formed even if there are few superconduction **** and superconduction thick films the magnitude of a substrate being two or more [100cm], and rocking or rotating a substrate preferably in an aspect of affairs besides the above.

[0061] This becomes possible to form each film also to two or more 100cm large area substrates.

[0062] After the process which forms the superconduction thick film of a single crystal preferably using a spreading thermal decomposition method forms a superconduction thick film with a spreading thermal decomposition method in top Norikazu and other aspects of affairs, it has the process made to single-crystal-ize by the laser annealing method.

[0063] By this technique, a superconduction thick film can be single-crystal-ized and a crystal stacking tendency can also be made good.

[0064] In top Norikazu and other aspects of affairs, the source of annealing in the laser annealing method is YAG (Yttrium-Aluminum Garnet) laser which has the excimer laser, or 0.5-micrometer or more wavelength of 2 micrometers or less which has 0.1-micrometer or more wavelength of 0.5 micrometers or less preferably.

[0065] Thus, the source of annealing can be chosen suitably. In top Norikazu and other aspects of affairs, four processings, a temporary-quenching join, a glost firing join, postannealing, and oxygen annealing, are preferably performed to a superconduction thick film at least.

[0066] The superconduction thick film which has a high superconduction property by this can be obtained. In top Norikazu and other aspects of affairs, the raw material in a spreading thermal decomposition method contains an organic metal raw material preferably.

[0067] Energy required for the deviation to an atom and a molecule required for formation of a superconduction thin film from an organic metal raw material is small by leaps and bounds as compared with the raw material which sintered and formed the mixture of the carbonate which is a raw material conventionally, or an oxide, or the raw material which contains melting and the single crystal made to solidify for them. For this reason, single crystal-ization of a superconduction thick film is attained in a comparatively simple heat treatment process by using an organic metal raw material. In addition, it is possible to use various kinds of acids of an organic system as a solvent.

[0068] In top Norikazu and other aspects of affairs, a superconduction thick film is preferably formed in both sides of a substrate.

[0069] Thereby, in a long wire rod or a large area substrate, a high superconduction property can be acquired by both sides.

[0070]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained based on drawing.

[0071] Drawing 1 is the sectional view showing roughly the configuration of the high-temperature superconductivity thick-film member in the gestalt of 1 operation of this invention. With reference to drawing 1, the high-temperature superconductivity thick-film member 5 has the substrate 1 which consists of a single crystal or polycrystal, the interlayer 2 of the single crystal nature formed on the main front face of a substrate, and the superconduction thick film 3 of the single crystal nature formed on the interlayer 2.

[0072] An interlayer 2 has the 0.1-micrometer or more thickness T2 of 3 micrometers or less, and the superconduction thick film 3 has 0.5-micrometer or more thickness T3 30 micrometers or less. The superconduction thick film 3 is formed by the spreading thermal decomposition method.

[0073] Rather than the coefficient of thermal expansion of a substrate 1, an interlayer 2 has a coefficient of thermal expansion near the coefficient of thermal expansion of the superconduction thick film 3, and has the lattice constant near [lattice constant / of a substrate 1] the lattice constant of the superconduction thick film 3.

[0074] The interlayer 2 has the structure which consists of crystal 2a which inclined aslant with the include angle theta of 10 degrees or less to the main front face of a substrate 1. Moreover, the angle of inclination of the stacking tendency within a field is 30 degrees or less. "The angle of inclination of the stacking tendency within a field" means the thing of "the peak-mesial-magnitude width of face in X-ray pole figure measurement", the peak in X-ray measurement will be so sharp that this value is small here, namely, the stacking tendency of a crystal will be good.

[0075] When a substrate 1 is a single crystal, as for the quality of the material of a substrate 1, it is desirable that they are the simple substance of sapphire, an ulmin acid lanthanum, magnesium oxide, and strontium titanate or the combination of such arbitration. Moreover, when a substrate 1 is polycrystal, as for the quality of the material of a substrate 1, it is desirable that it is the simple substance of stainless steel, Hastelloy, nickel, copper, and aluminum or the combination of such arbitration, and is the flexible metal which has the thickness of 200 micrometers or less.

[0076] Moreover, as for the middle class's quality of the material, it is desirable that it is the multilayer structure of the monolayers of the single element system oxides chosen from the zirconium, the ytterbium, the yttrium, and the cerium or those multiple oxides, those single element systems, or the multi-element system matter.

[0077] In addition, as shown in drawing 2, superconduction **** 4 of single crystal nature may be formed between the interlayer 2 and the superconduction thick film 3, and as shown in drawing 3, superconduction **** 4 of single crystal nature may be formed between the substrate 1 and the superconduction thick film 3 instead of the interlayer 2.

[0078] Although the quality of the material of superconduction **** 4 and the quality of the material of the superconduction thick film 3 which are shown in drawing 2 and drawing 3 may be the same, it is desirable that a RE (rare earth) element different mutually [have both REBCO123 structures and] is included as a configuration element. Moreover, it is desirable that the quality of the material of superconduction **** 4 is chosen so that the melting point of superconduction **** 4 may become higher than the melting point of the superconduction thick film 3.

[0079] Moreover, as for the quality of the material of the superconduction thick film 3, it is desirable that have REBCO123 structure and RE (rare earth) element contains a holmium.

[0080] Next, the manufacture approach of the gestalt this operation is explained. Drawing 4 is drawing showing the manufacture approach of the high-temperature superconductivity thick-film member in the gestalt of 1 operation of this invention. With reference to drawing 4, the substrate 1 which consists of a single crystal or polycrystal first is prepared, and an interlayer 2 is formed on the substrate 1 (step S1). Then, the superconduction thick film 3 is formed by the spreading thermal decomposition method, and the high-temperature superconductivity thick-film member 5 is manufactured. In this spreading thermal decomposition method, the solution which melted the organic metal compound which is an organic

metal raw material first to the organic solvent is prepared (step S2). Then, the thick film of a metal content compound is formed by drying, after applying the solution on an interlayer 2 (step S3). By carrying out heating baking of the thick film of this metal content compound, the superconduction thick film 3 is formed (step S4), and the high-temperature superconductivity thick-film member 5 is obtained. [0081] An interlayer 2 is formed by 0.1-micrometer or more thickness of 3 micrometers or less, and the superconduction thick film 3 is formed by 0.5-micrometer or more thickness of 30 micrometers or less.

[0082] In addition, it is after an interlayer's 2 formation process (step S1), and it is desirable that superconduction **** 4 of the single crystal nature which consists of the different quality of the material from the superconduction thick film 3 before the formation process (step S2 - S4) of a superconduction thick film is formed by physical vapor deposition on an interlayer 2.

[0083] Moreover, as for an interlayer 2, being formed by physical vapor deposition is desirable, and it is [this physical vapor deposition] desirable that it is the laser ablation method to make the matter which irradiated laser light at the raw material and dispersed from the raw material vapor-deposit on the main front face of a substrate. Furthermore, as for this laser ablation method, it is desirable to be carried out after the main front face of a substrate 11 has inclined to the field where the laser light 13 of a raw material (target) 11 is irradiated as shown in drawing 5 only in the predetermined include angle alpha. In this case, the predetermined part of a substrate 1 may be covered with the mask 12.

[0084] As a process of this substrate inclination laser vacuum deposition (drawing 5) For example, ablation is produced by extracting a beam by optical system and irradiating the laser light 13 with the energy density of 1 - 5 J/cm² to the sintered compact target 11 in the hypoxia ambient atmosphere of 100mTorr extent, in order to realize laser light of high density using an excimer laser. Making a substrate 1 heat, when the AZUDEPO film is generated and membranes are formed by applying the plasma produced in ablation to a substrate 1, fundamental single crystal nature structure is formed.

[0085] By forming an interlayer 2 using such physical vapor deposition, oxides, such as yttria stabilized zirconia (YSZ) and cerium oxide (CeO₂), can be formed on the flexible metal substrate 1 excellent in the oxidation resistance of Hastelloy, heat-resistant stainless steel, etc.

[0086] moreover, except for the membrane formation approaches other than laser vacuum deposition -- chemical vapor deposition, such as physical vapor deposition, such as a spatter and an electron beam, and CVD (Chemical Vapor Deposition), and MOD (Metal Organic Deposition) -- solution methods, such as law, etc. may be used. Moreover, after an interlayer 2 may be formed of a spreading thermal decomposition method independent or is formed by the spreading thermal decomposition method, by the laser annealing method, it may crystallize single and he may be formed.

[0087] In addition, in drawing 4 , superconduction **** 4 may be formed instead of an interlayer 2 (step S1), and the superconduction thick film 3 will be formed on superconduction **** 4 in this case (step S2 - S4).

[0088] About the quality of the material of this superconduction **** 4, although not limited, a configuration element serves as a candidate for application with most desirable YBCO123 structure or REBCO123 structure, when the property of 77K is considered. As a process of laser vacuum deposition, for example in the case of the superconduction thin film of YBCO123 structure and REBCO123 structure In the hypoxia ambient atmosphere of 100mTorr extent, using an excimer laser, because extract a beam by optical system and 1-5J /irradiates laser with the energy density of 2 cm to a sintered compact target, in order to realize laser light of high density Ablation is produced, and making about 600-800 degrees C heat a substrate, when the AZUDEPO film is generated and membranes are formed by applying the plasma produced in ablation to a substrate, the crystal structure of fundamental superconduction is formed.

[0089] In addition, as an approach of forming the superconduction thick film of a single crystal using a spreading thermal decomposition method, after forming a superconduction thick film with a spreading thermal decomposition method, the technique made to single-crystal-ize by the laser annealing method may be taken.

[0090] As a class of concrete laser used for the laser annealing method, it is realistic that they are an excimer laser and an YAG laser. Although the wavelength of an excimer laser changes also with classes

of the gas to be used, it is 0.1 micrometers or more 0.5 micrometers or less. In detail, 308nm can be realized by 248nm and XeCl, 157nm and ArF have realized [F2] 351nm by XeF at 193nm and KrF, and the peak price of the present condition of an output is 150W to 200W. The wavelength of an YAG laser is 0.5 micrometers or more 2 micrometers or less, and is 1.06 micrometers typically. Development of high-power-izing and a long duration-ized oscillation is progressing quickly with progress of a semiconducting crystal in recent years, and, as for the YAG laser, the thing with an output of 3kW is sold also for this time by LD excitation. As high power laser, of course, it is not limited to YAG and carbon dioxide laser (10.6 micrometers) etc. can also be applied. Moreover, if short wavelength laser can also use the laser of hundreds ofW class not only by the excimer laser but by 0.5 micrometers or less, it will not be limited to an excimer laser.

[0091] moreover, the substrate 1 -- a line (the shape of a tape is included) -- by twisting one end around a roll 21 on the other hand, and rolling round another side one end with a roll 22, as shown in drawing 6, the middle class 2 or superconduction **** 4 may be formed on a substrate 1 within a chamber 23, and the superconduction thick film 3 may be formed in a case within a chamber 24.

[0092] Moreover, when the magnitude of a substrate 1 is two or more [100cm], it is desirable that an interlayer 2, or superconduction **** 4 and the superconduction thick film 3 is formed, making it rotate, as a substrate 1 is made to rock so that it may be shown in the direction of an arrow head of drawing 7 or the arrow head of drawing 8 shows.

[0093] In addition, it is desirable that four processings, a temporary-quenching join, a glost firing join, postannealing, and oxygen annealing, are performed to the superconduction thick film 3 at least, and the superconduction thick film 3 may be formed in both sides of a substrate 1.

[0094]

[Example] Hereafter, the example of this invention is explained.

[0095] (Example 1) The middle class of cerium oxide was formed by the laser ablation method on the sapphire single crystal substrate. An interlayer's thickness was 1 micrometer.

[0096] The superconduction thick film expressed with a spreading thermal decomposition method with the presentation of YBa₂Cu₃O_{7-d} was formed on this interlayer. The start raw material prepared what melted the naphthenate of each element to the ethanol solvent so that the presentation ratio of Y:Ba:Cu might be set to 1:2:3, and it formed the superconduction thick film by giving spreading, heat treatment, and oxygen annealing. Thickness and critical current density were measured about the formed superconduction film. The relation between the thickness of the superconduction film and critical current density is shown in Table 1.

[0097]

[Table 1]

超電導膜の膜厚 (μm)	0.1	0.5	1	5	10	30	50	100
臨界電流密度 (MA/cm^2)	0.2	2.0	3.5	3.0	2.4	1.8	0.5	0.1

[0098] From the result of Table 1, after forming an interlayer predetermined by the laser ablation method, when forming the superconduction thick film with the spreading thermal decomposition method, it became clear that the superconduction property which was excellent in 0.5-micrometer or more superconduction thick film 30 micrometers or less is acquired.

[0099] (Example 2) The middle class of cerium oxide was formed by the laser ablation method on the sapphire single crystal substrate. An interlayer's thickness was 1 micrometer. Superconduction **** which uses the laser ablation method and is expressed with the presentation of YBa₂Cu₃O_{7-d} on this middle class was formed. The thickness of superconduction **** was 1 micrometer.

[0100] Furthermore, the superconduction thick film expressed with a spreading thermal decomposition method with the presentation of YBa₂Cu₃O_{7-d} was formed on this superconduction ****. The start raw

material prepared what melted the naphthenate of each element to the ethanol solvent so that the presentation ratio of Y:Ba:Cu might be set to 1:2:3, and it formed the superconduction thick film by giving spreading, heat treatment, and oxygen annealing. Thickness and critical current density were measured about the formed superconduction film. The relation of the thickness of the superconduction film and critical current density which were formed in Table 2 with the spreading thermal decomposition method is shown.

[0101]

[Table 2]

超電導膜の膜厚 (μm)	0.1	0.5	1	5	10	30	50	100
臨界電流密度 (MA/cm^2)	0.5	3.0	4.3	4.5	3.0	2.4	0.6	0.2

[0102] After forming the middle class predetermined by the laser ablation method, when forming superconduction **** by the laser ablation method and forming the superconduction film with the spreading thermal decomposition method on it further from the result of Table 2, it became clear that the superconduction property which was excellent in 0.5-micrometer or more superconduction thick film 30 micrometers or less is acquired.

[0103] (Example 3) The middle class of cerium oxide was formed by the laser ablation method on the sapphire single crystal substrate. An interlayer's thickness was 1 micrometer. Superconduction **** which uses the laser ablation method and is expressed with the presentation of YBa₂Cu₃O_{7-d} on this middle class was formed. The thickness of superconduction **** was 1 micrometer.

[0104] On this superconduction ****, the solution which melted the naphthenate of each element to the ethanol solvent so that the presentation ratio of Y:Ba:Cu might be set to 1:2:3 as a start raw material was prepared and applied. When laser was furthermore irradiated in this applied field, the solvent of a spreading side was removed, crystallization took place, and the superconduction thick film has been formed. The laser used at this time is a KrF excimer laser with a wavelength of 248nm, and irradiated the spreading side by 2 the laser energy consistency of 0.1J/cm. Thickness and critical current density were measured about the superconduction film formed by this laser radiation. The relation between the thickness of the superconduction film and critical current density is shown in Table 3.

[0105]

[Table 3]

超電導膜の厚み (μm)	0.1	0.5	1	5	10	30	50	100
臨界電流密度 (MA/cm^2)	0.1	1.7	3.1	2.7	2.5	1.6	0.4	0.1

[0106] After forming the middle class predetermined by the laser ablation method, when forming superconduction **** by the laser ablation method, carrying out laser radiation to what applied the solution of a superconducting material on it further and forming the superconduction film from the result of Table 3, it became clear that the superconduction property which was excellent in 0.5-micrometer or more superconduction thick film 30 micrometers or less is acquired.

[0107] (Example 4) On the sapphire single crystal substrate, what melted the naphthenate of a cerium to the ethanol solvent was applied, and the interlayer of cerium oxide was formed by performing heat treatment and oxygen annealing treatment. An interlayer's thickness was 1 micrometer. Superconduction **** which uses the laser ablation method and is expressed with the presentation of YBa₂Cu₃O_{7-d} on this middle class was formed. The thickness of superconduction **** was 1 micrometer.

[0108] On this superconduction ****, the superconduction thick film expressed with a spreading

thermal decomposition method with the presentation of YBa₂Cu₃O_{7-d} was formed. The start raw material prepared what melted the naphthenate of each element to the ethanol solvent so that the presentation ratio of Y:Ba:Cu might be set to 1:2:3, and the superconduction thick film was formed by giving spreading, heat treatment, and oxygen annealing. Thickness and critical current density were measured about the superconduction film formed with the spreading thermal decomposition method. The relation between the thickness of the superconduction film and critical current density is shown in Table 4.

[0109]

[Table 4]

超電導膜の膜厚 (μm)	0.1	0.5	1	5	10	30	50	100
臨界電流密度 (MA/cm^2)	0.1	1.5	3.0	2.6	2.1	1.5	0.3	0.1

[0110] After forming the middle class predetermined with a spreading thermal decomposition method, it became clear from the result of Table 4 that the superconduction property which was excellent in 0.5-micrometer or more superconduction thick film 30 micrometers or less is acquired by forming superconduction **** by the laser ablation method, and forming the superconduction film with a spreading thermal decomposition method on it further.

[0111] (Example 5) Superconduction **** which uses the laser ablation method and is expressed with the presentation of YBa₂Cu₃O_{7-d} on an ulmin acid lanthanum single crystal substrate was formed. The thickness of superconduction **** was 1 micrometer.

[0112] Furthermore, the superconduction thick film expressed with a spreading thermal decomposition method with the presentation of YBa₂Cu₃O_{7-d} was formed on this superconduction ****. The start raw material prepared what melted the naphthenate of each element to the ethanol solvent so that the presentation ratio of Y:Ba:Cu might be set to 1:2:3, and the superconduction thick film was formed by giving spreading, heat treatment, and oxygen annealing. Thickness and critical current density were measured about the formed superconduction film. The relation of the thickness of the superconduction film and critical current density which were formed in Table 5 with the spreading thermal decomposition method is shown.

[0113]

[Table 5]

超電導膜の膜厚 (μm)	0.1	0.5	1	5	10	30	50	100
臨界電流密度 (MA/cm^2)	0.5	3.5	4.8	4.9	3.7	3.2	0.7	0.3

[0114] It became clear from the result of Table 5 that the superconduction property which was excellent in 0.5-micrometer or more superconduction thick film 30 micrometers or less is acquired by forming superconduction **** by the laser ablation method, and forming the superconduction film with a spreading thermal decomposition method on it further.

[0115] It should be thought that the gestalt and example of operation which were indicated this time are [no] instantiation at points, and restrictive. The range of this invention is shown by the above-mentioned not explanation but claim, and it is meant that all modification in a claim, equal semantics, and within the limits is included.

[0116]

[Effect of the Invention] Although the high-temperature superconductivity thick-film member according to 1 and other aspects of affairs of this invention is effective in especially obtaining the volume

efficiency of a thin film wire rod or the large area film as stated above, it is suitable also for the repair technique of a long yttrium system wire rod, for example. For example, even if it produces a long wire rod on a metal substrate, the part where a property is low is generated partially, but if this invention is used, the superconduction film can be formed in the part and this invention is effective also in an improvement of a rate-limiting process.

[0117] Moreover, the film of a large area is required of application to a current limiter etc. Generally, with physical vapor deposition, since the area which can form membranes at once is small, in order to acquire a uniform high property by low cost industrially, it is necessary to enlarge vacuum evaporation area. This invention serves as technique also suitable for formation of the large area film by combining rocking and rotation of a substrate.

[0118] In this invention, the wire rod or large area film formed through the interlayer on a flexible metal substrate or a single crystal, polycrystal, or a metal substrate serves as a desirable object. If a high current can be passed with the long wire rod on a flexible metal substrate, the impact given to industrial ways, such as a cable and a magnet, is very large. Moreover, even if it compares with bismuth system silver covered-wire material, if it is under the environment cooled and used or less for 77K by cooling of supercooling nitrogen or a refrigerator, although a magnetic field property is based also on magnetic field strength as compared with bismuth system silver covered-wire material, it is large [the critical current density / the critical current density J_c under the magnetic field of 77K is high by leaps and bounds and] at the order which is about single figure. For this reason, if that mass-production nature becomes possible as a charge of real material, even if it will exceed an about single figure bismuth system silver covering superconduction wire rod in cost, a cost merit comes out.

[0119] Moreover, in bismuth system silver covered-wire material, the device application which cannot be attained also becomes possible. For example, installation of the dependability of the electric power system to which decentralization will progress from now on [since the diversification of risks at the time of the occurrence of the network accident by thunderbolt etc. if mass production method becomes / the yttrium system film which cannot build SN rearrangement mold current limiter by bismuth system silver covered-wire material, and has a large area / possible in a low cost and high homogeneity property is attained] not only increasing by leaps and bounds but a decentralization power source may also be promoted effectively.

[Translation done.]